0   1989

TITLE OFF-DIAGONAL COULOMB INTERACTIONS IN THE EXTENDED PEIERLS-HUBBAND MODEL: EXACT DIAGONALIZATION RESULTS

AUTHOR(S) David K. Campbell
Tinka Gammel
E. Y. Loh

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

OFF-DIAGONAL COULOMB INTERACTIONS IN THE EXTENDED PEIERLS-HUBBARD MODEL: EXACT DIAGONALIZATION RESULTS

D.K. Campbell, J. Tinka Gammel, E.Y. Loh, Jr.,
Theoretical Division and Center for Nonlinear Studies,
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

INTRODUCTION

As evidenced by the many contributions to these proceedings, the role of electron-electron interactions in solid-state systems continues to be the subject of intense investigation and debate. Much of the recent discussion has been stimulated by experimental work on exciting novel materials, including high-temperature superconducting copper oxides, "heavy-fermion" systems, organic synthetic metals, and halogen-bridged transition-metal chains. Unlike conventional metals, for which standard single-electron (band) theories describe quantitatively the electronic structures and excitations, these new materials are currently thought to have properties dominated by many-body effects arising from strong electron-electron interactions. It is essential to have tractable models that capture the essence of both electron-phonon (e-p) and electron-electron (e-e) interactions and that represent faithfully their synergetic, or competing, effects.

For conjugated polymers, the extended Peierls-Hubbard model has been widely accepted as correctly incorporating the effects of both e-p and e-e interactions. In the absence of e-e interactions, the ground state of $(CH)_x$ is the $2k_F$ bond-order wave (BOW) — dimerization/bond alternation — predicted by Peierls theorem. It is now well established [1] that for the weak e-p coupling appropriate to $(CH)_x$, the on-site Coulomb repulsion actually enhances dimerization up to fairly large values ($U > 6t_0$). These results are still widely regarded as counter to the conventional wisdom that Coulomb interactions should suppress the build-up of charge anywhere, on the sites or on the bonds. Since the extended Peierls-Hubbard model incorporates only (lattice) site-diagonal parts of the electron-electron interactions (U, V), and omits the off-diagonal bond-charge repulsions (W, X), it is natural to ask whether this model adequately describes the full consequences of e-e interactions. In the specific context of $(CH)_x$, the potential importance of this omission is readily recognized [2]. Intuitively, the bond charge repulsion should suppress dimerization, since it opposes the build up of charge on the bonds. Thus, the absence of W and X terms in the standard extended Peierls Hubbard models suggests a priori that these models may artificially favor the continuation of dimerization in the half filled band into the region of intermediate to strong Coulomb interaction.

More generally, the omission of terms such as W and X raises significant questions about the appropriateness of Hubbard models for describing e-e interactions in the

whole class of novel solid state materials. Thus this issue is extremely important and must be investigated in a thorough and definitive manner.

MODEL

To analyze the effects of off-diagonal Coulomb terms in quasi-one-dimensional systems, we consider the modified Peierls-Hubbard Hamiltonian containing all nearest neighbor interactions [2,3,4,5]

$$H = -\sum_{\ell}(t_0 - \alpha\delta_\ell)B_{\ell,\ell+1} + \frac{K}{2}\sum_{\ell}\delta_\ell^2 + U\sum_{\ell}n_{\ell\uparrow}n_{\ell\downarrow} + V\sum_{\ell}n_\ell n_{\ell+1}$$
$$+ X\sum_{\ell}B_{\ell,\ell+1}(n_\ell + n_{\ell+1}) + W\sum_{\ell}(B_{\ell,\ell+1})^2 \quad . \tag{1}$$

where $n_{\ell\sigma} = c_{\ell\sigma}^\dagger c_{\ell\sigma}$ and $B_{\ell,\ell+1} = \sum_\sigma(c_{\ell\,\sigma}^\dagger c_{\ell+1\,\sigma} + c_{\ell+1\,\sigma}^\dagger c_{\ell\,\sigma})$. In H, t_0 is the hopping integral for the uniform lattice, α is the electron-phonon coupling, δ_ℓ is the relative displacement between the ions at sites ℓ and $\ell+1$, K represents the cost of distorting the lattice, and U, V, X, and W model the electron-electron interactions. U represents the on-site Coulomb repulsion, and V the nearest-neighbor repulsion. X is a "mixed" term involving both on-site and bond-charge effects, and W is the pure bond-charge repulsion. The presence of such terms follows directly from the original many-body Hamiltonian, including Coulomb interactions; the explicit derivations are available in the literature [2,5,6,7]. U, V, and all the longer-ranged diagonal terms will always contain contributions dependent only on the range of the electron-electron potential, whereas W and X are suppressed by the atomic orbital overlap. This is the origin of the familiar result that for narrow bands the diagonal Coulomb terms are dominant. However, even if the band is not narrow, if the potential is not strongly screened, one still expects the diagonal terms to be more important numerically than the off-diagonal terms. When the off-diagonal terms are not *a priori* negligible, the central issue is the extent to which they produce results qualitatively different from those predicted in their absence. To answer this question correctly, it is clear that whatever the relative values of V, X, and W one must anticipate that $U > V, X, W$ and hence must adopt a method that gives correct results in this parameter regime. Since in many materials one expects $U \simeq 4t_0$, to be certain of the results one should use (numerically) exact many-body methods known to be reliable in the intermediate-coupling regime, though examining various limiting cases gives useful insight into the exact results. Indeed, to gain insight into our later exact diagonalization results, we begin with an analysis of the strong-coupling limit.

STRONG COUPLING PERTURBATION THEORY

In the limit that $U \to \infty$, double occupancy of any site is energetically not allowed. The resultant spin-Peierls Hamiltonian [1b,8] is

$$H_{eff} = \frac{K}{2}\sum_\ell\delta_\ell^2 + X \cdot V + \sum_\ell\left(\frac{t_{\ell,X}^2}{U - V} - W\right)(4\vec{S}_\ell \cdot \vec{S}_{\ell+1} - 1) \tag{2}$$

where $t_{\ell,X} = ((t_0 - 2X - \alpha\delta_\ell)$. The first effect of W, then, is to suppress antiferromagnetism. Further, to lowest order in δ_ℓ, the spin coupling is proportional to

$$t_{\ell,X}^2 - W(U - V) \sim t_0'^2 - 2\alpha't_0'\delta_\ell + O(\delta_\ell^2) ,$$

where $t_0' \equiv \sqrt{(t_0 - 2X)^2 - W(U - V)}$ and $\alpha' = \alpha(t_0 - 2X)/t_0'$. For given t_0 and X, since the effective t_0' decreases with W, the effective electron-phonon coupling $\pi\lambda' \equiv 2\alpha'^2/Kt_0'$ increases with W due both to the increase in α' and the decrease in t_0'. This leads to the initially surprising conclusion that, for large U, the dimerization should initially increase with W, the bond-charge repulsion.

When W reaches a critical value $W_c \simeq (t_0 - 2X)^2/(U - V)$, the spin coupling becomes ferromagnetic. The spins will then tend to align, forming a ferromagnetic SDW with $4\vec{S}_\ell \cdot \vec{S}_{\ell+1} \simeq 1$. The minimum energy configuration then has $\delta_\ell = 0$, and the ground state is an undimerized ferromagnetic SDW. The resulting phase diagram is shown in Fig. 1a.

Fig. 1. The phase diagram as a function of V/t and W/t for intermediate coupling $U = 4t = 4t_0 - 8X$ (a) from strong-coupling perturbation theory and (b) for the half-filled dimer.

ANALYTIC RESULTS FOR A DIMER

The "dimer" two electrons on two sites provides surprisingly accurate insight into many aspects the behavior of larger systems. For comparison with the numerical results, we use periodic boundary conditions, so that $c_3^+ = c_1^+$ and similarly for all other operators. The Hamiltonian in (1) then assumes the explicit form

$$
\begin{aligned}
H_d = -2t_0 B_{1,2} + U(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}) + 2Vn_1 n_2 \\
+ 2X B_{1,2}(n_1 + n_2) + 2W(B_{1,2})^2 .
\end{aligned}
\tag{3}
$$

Since there is no possibility of bond alternation with only one bond, no explicit electron-phonon coupling appears. Further, one has $n_1 + n_2 \equiv 2$; thus just as in the case of the $U \to \infty$ limit, the X term simply renormalizes the hopping to $t \equiv t_0 - 2X$.

Simple counting shows that there are six possible states for two electrons on two sites. As basis states we choose

$$
|1,1\rangle = c_{2\uparrow}^+ c_{1\uparrow}^+|0\rangle, \quad |1,-1\rangle = c_{2\downarrow}^+ c_{1\downarrow}^+|0\rangle, \quad |1,0\rangle = \frac{1}{\sqrt{2}}(c_{2\downarrow}^+ c_{1\uparrow}^+ + c_{2\uparrow}^+ c_{1\downarrow}^+)|0\rangle,
$$

$$
|0,0\rangle = \frac{1}{\sqrt{2}}(c_{2\downarrow}^+ c_{1\uparrow}^+ - c_{2\uparrow}^+ c_{1\downarrow}^+)|0\rangle,
$$

$$
|S\rangle = \frac{1}{\sqrt{2}}(c_{1\downarrow}^+ c_{1\uparrow}^+ + c_{2\downarrow}^+ c_{2\uparrow}^+)|0\rangle, \quad |A\rangle = \frac{1}{\sqrt{2}}(c_{1\downarrow}^+ c_{1\uparrow}^+ - c_{2\downarrow}^+ c_{2\uparrow}^+)|0\rangle.
$$

As the notation suggests, the first three states are, respectively, the $S_z = +1, -1$, and 0 components of the spin triplet state and, by the spin symmetry of H, must all have the same energy. The state $|0,0>$ is a spin-singlet made entirely from singly-occupied states, while $|S>$ and $|A>$ are, respectively, spin-singlets made from symmetric and antisymmetric combinations of the two states involving double occupancy. Trivial algebra leads to the following results: (1) the triplet states are degenerate eigenstates of H_d, with eigenvalue $E_T = 2V$; (2) the state $|A>$ is also an eigenstate, with eigenvalue U; and (3) the states $|0>$ and $|S>$ are coupled, with the two eigenvalues $E_\pm = 8W + U/2 + V \pm \Delta/2$ where $\Delta = ((U - 2V)^2 + (8t_0 - 16X)^2)^{1/2}$. The ground state "phase diagram" for the dimer follows immediately by comparing these eigenenergies. For $U \equiv U = 4t$ (intermediate coupling), this diagram as a function of W/t and V/t is shown in Fig. 1b. For small values of W, the state E_- is always the ground state. This state, which in the absence of e-e interactions is just the $k = 0$ band state, corresponds to the "dimerized/BOW" phase and indeed, in the larger systems shows non-zero values of the dimerization. In the region bounded by AB and BC, the triplet state is the ground state: this corresponds to the ferromagnetic SDW phase found in larger systems. Finally, in the region bounded by BC and BD, the ground state is the state $|A>$; this corresponds to the CDW phase in larger systems.

EXACT DIAGONALIZATION: RESULTS AND DISCUSSION

In the region of intermediate e-e coupling anticipated to apply to many novel materials, we have calculated numerically the "exact" ground state of 4, 6, 8, and 10 site rings described by the Hamiltonian (1) using a version of the Lanczos method [9]; details will be published elsewhere [5]. We use the conventional SSH-polyacetylene parameters $\alpha = 4.1 \text{eV}/\text{Å}, K = 21 \text{eV}/\text{Å}^2$, and $t_0 = 2.5 \text{eV}$. We focus on the phase diagram as a function of W and V at fixed $U = U_0$. Surprisingly, even for intermediate coupling the primary effect of X is merely to renormalize t_0. The details of results including the X term are reported elsewhere [5].

Fig. 2 shows the phase diagram for an 8-site ring; comparison with 4-, 6-, and 10-site results, as well as the analytic strong coupling and dimer predictions, suggests this diagram reflects the infinite-ring behavior. The phase boundaries in Fig. 2 in general reflect a "first order transition" in the dimerization order parameter, δ_0: that is, there is a sudden qualitative change in the nature of the ground state, and δ_0 drops almost immediately from a finite value to zero. However, for short segment of the BOW/CDW boundary near $W = 0$ --- the range is roughly $0 < W < 0.1$ --- the transition becomes second order. Except for this short segment, the dimerized phase has non-zero dimerization on its boundary.

In Figs. 3 and 4 we show the optimal dimerization δ_0 versus W when $U_0 = 4t_0 (= 10 \text{eV})$, $V = 0$ and $V = 3 \text{eV}$, respectively. Note the distinction between "Jahn-Teller" ($4N$) and "non-Jahn-Teller" ($4N + 2$) systems persists even away from the band theory limit. It also suggests that systems with $N \geq 8$ are near the converged large N behavior. Incidentally, the dotted regions of the 4-site ring results reflect the dimerization observed in the BOW phase. However, the actual ground state of the 4-site system at values of W in these dotted regions is a different, small-ring phase, which does not appear in the larger rings. Thus the solid line for the 4-site system, which shows the dimerization going to zero at relatively small values of W, although strictly correct, is essentially an artifact of the small system size. The dotted line, which explicitly ignores this small-ring phase and plots the dimerization assuming the BOW state remains the ground state until the transition to a ferromagnetic SDW, shows more clearly the true finite size effects on W_c and δ_0 vs. W.

Fig. 2 (left): The phase diagram as a function of V/t_0 and W/t_0 for intermediate coupling $U = 4t_0 = 10eV$, and $X = 0$. Phase boundaries are plotted for a 8-site ring. The ground-state changes discontinuously across solid lines, smoothly across the dotted line.

Fig. 3 (right): Dimerization as a function of W/t_0 for $U = 4t_0 = 10eV$ and $V, X = 0$ for 4-, 6-, 8-, and 10-site rings. For the 4-site ring, the dotted line gives results for the lowest energy dimerized state even though for this small ring the ground state is not dimerized for intermediate values $(0.10 < W/t_0 < 0.225)$ of W/t_0.

Fig. 4 (left): Dimerization as a function of W/t_0 for $U = 4t_0 = 10eV$, $V = 3eV$, and $X = 0$ for 4-, 6-, 8-, and 10-site rings. The 4-site ring is not dimerized for intermediate values $(0.16 < W/t_0 < 0.29)$ of W/t_0.

Fig. 5 (right): Bond-charge measurements on the 8-site ring as a function of W/t_0 for $U = 10eV$ and $V = 0$: a) bond-charge correlation (multiplied by 1/2), b) average bond charge, and c) alternating bond charge, which is proportional to the dimerization.

The dimerized/BOW phase persists for a substantial range of Coulomb repulsion, both diagonal and off-diagonal. Indeed, dimerization increases monotonically with W before dropping rapidly to zero in a "first order phase transition" at $W = W_c$ in agreement with the strong coupling arguments above. In particular, as shown in Fig. 3, even for $V = 0$, W does not destroy dimerization until $W_c = 0.6eV \simeq 0.25t_0$. For $0 < V < U_0/2$, the dimerized phase persists until still larger values of W, and again W increases dimerization (slightly) until the BOW/FM SDW boundary is reached (Fig. 4). Note the increase in W_c relative to $V = 0$ as expected from the strong coupling arguments above. The existence of real materials with $W > W_c$ remains an open question; it is conceivable that the recently observed organic ferromagnetic materials may be modeled using parameters in this range. However, for $(CH)_x$ and the other conjugated polymers, the experimentally observed dimerization requires, within the model Hamiltonian, $W < W_c$. Importantly, one still finds dimerization for strong, internally consistent Coulomb interactions; the assumption of weak e-e interactions is not required. This is fortunate, for in the case of $(CH)_x$, such an assumption appears inconsistent with both observed spin density ratios [10] and optical absorption involving neutral and charged solitons [1f].

Increasing W, of course, must suppress bond-charge correlations. In Fig. 5, the bond-charge correlation, average bond charge, and alternating bond charge are plotted as a function of W for intermediate coupling, $U_0 = 4t_0$ and $V = 0$, on the 8-site ring. As expected, the bond-charge correlation, $\langle B^2 \rangle = \frac{1}{N} \sum B_{l,l+1}^2$, which couples directly to W in the Hamiltonian, is suppressed monotonically as W is turned on. Counter to simple intuition, however, the average bond charge, $\langle B \rangle = \frac{1}{N} \sum B_{l,l+1}$, does not fall off as dramatically as the correlation and indeed, for small W, the bond charge stays remarkably flat. Meanwhile, the alternating bond charge, which is related to the dimerization by $\langle B' \rangle = \frac{1}{N} \sum (-)^l B_{l,l+1} = K\delta/\alpha$, increases with W, as we have seen earlier. In sum, although W does suppress bond-charge correlations, the effects on average and alternating bond charge are quite different, and, in particular, we observe that W enhances the dimerization.

Although the off-diagonal terms produce only minor quantitative effects on dimerization, for other observables they can have important qualitative consequences. The mixed bond-site term X breaks charge conjugation/particle-hole symmetry; its inclusion in models of $(CH)_x$ may thus help explain the puzzling "intensity anomaly" in polaron/bipolaron optical absorption [11] experiments and also the ratio of neutral ($S^\circ - S^\circ$) to charged ($S^+ - S^-$) soliton pairs in the decay channels of electron-hole pairs in photo-excitation of trans-$(CH)_x$ [1f]. In both these cases, the X term may well be more important than the straightforward next-nearest neighbor hopping term, t_2; within a tight-binding model, $t_2 \propto e^{-\kappa_0 a} t_0$. Further, when X terms are included in H, the hopping in effect acquires a band-filling dependence; this may be quite significant in applying Hubbard-like models to situations other than the half-filled band.

Finally, we turn to the general issue of the applicability of the standard Hubbard model. Here it is useful to place our work in the context of several recent articles that, in one way or another, have revisited the original analyses [6,7,12] that justified the "zero differential overlap" approximation that neglects off-diagonal terms. The simple, intuitive arguments for e-e interactions suppressing dimerization, based on first-order weak-coupling perturbation theory [2], are not born out by more detailed calculation. Although our study focused explicitly on a (numerically) exact solution for) short-ranged Coulomb effects, involving only on-site and nearest neighbor interactions, our results are consistent with two recent variational studies [13] involving (approximate) solutions for the full (screened) Coulomb interaction. For the expected region of parameters, the variational results on the full Coulomb problem are consistent with early (Gutzwiller) variational calculations in the pure Hubbard model [14]. In summary, the

familiar Hubbard and extended Hubbard models remain valid and useful theoretical starting points for understanding the role of electron-electron interactions in a variety of novel real materials.
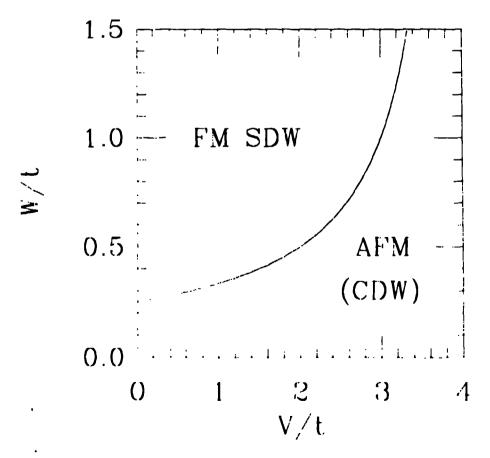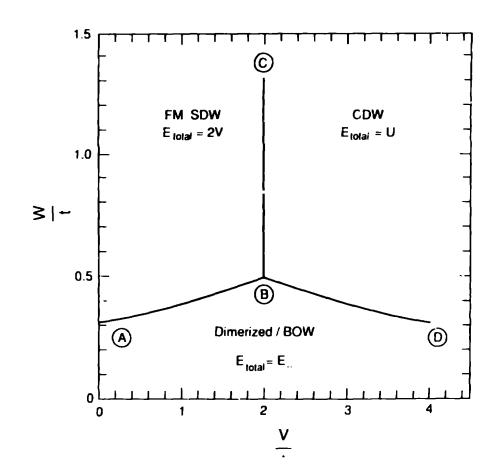
ACKNOWLEDGEMENTS

REFERENCES

1. Recent studies of the extended Peierls-Hubbard models include:
   (a) S. Mazumdar and S.N. Dixit, Phys. Rev. Lett., 51 (1983) 292 and Phys. Rev. B, 29 (1984) 1824; (b) J.E. Hirsch, Phys. Rev. Lett., 51 (1983) 296; (c) Z.G. Zoos and S. Ramasesha, ibid, 51 (1983) 2374; (d) D. K. Campbell, T. A. DeGrand, and S. Mazumdar, ibid, 52 (1984) 1717; (e) J. E. Hirsch and M. Grabowski, ibid, 52 (1984) 1713; (f) W.K. Wu and S. Kivelson, Phys. Rev. B, 33 (1986) 8546; S. Kivelson and W.K. Wu, ibid, 34 (1986) 5423; (g) S. Kivelson and D.E. Heim, ibid, 26 (1982) 4278.

2. S. Kivelson, W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett., 58 (1987) 1899.

3. D. Baeriswyl, P. Horsch, and K. Maki, Phys. Rev. Lett., 60 (1988) 70.

4. J. T. Gammel and D. K. Campbell, Phys. Rev. Lett., 60 (1988) 71.

5. D.K. Campbell, J.T. Gammel, and E.Y. Loh, Jr., Phys. Rev. B, 38 (1988) 12043 (RC); and to be published. Synthetic Metals, 27, (1988) A9.

6. J. Hubbard, Proc. Roy. Soc. London A, 276 (1963) 238.

7. R.G. Parr, J. Chem. Phys., 20 (1952) 1499; R. Pariser and R.G. Parr, ibid, 21 (1953) 767; J.A. Pople, Proc. Roy. Soc. London A, 68 (1955) 81.

8. J.W. Bray, L.V. Interrante, I.S. Jacobs, and J.C. Bonner, in "Extended Linear Chain Compounds", edited by J.S. Miller, Plenum, New York, 1983, Vol. 3, p. 355.

9. See, e.g., the section on Lanczos diagonalization in Pissantsky, "Sparse Matrix Technology", London; Orlando, Academic, 1984.

10. A.J Heeger and J.R. Schrieffer, Sol. St. Comm., 48 (1983) 207; H. Thomann, L.R. Dalton, M. Grabowski, and T.C. Clarke, Phys. Rev. B, 31 (1985) 3141.

11. K. Fesser, A.R. Bishop and D.K. Campbell, Phys. Rev. B, 27 (1983) 4804.

12. L. Salem, "Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966; R.G. Parr, D.P. Craig, and I.G. Ross, J. Chem. Phys., 18 (1950) 1561.

13. C. Wu, X. Sun, and K. Nasu, Phys. Rev. Lett., 59 (1987) 831; A. Painelli and A. Girlando, submitted to Solid State Commun.; Synthetic Metals, 27, (1988) A15.

14. D. Baeriswyl and K. Maki, Mol. Cryst. Liq. Cryst., 118 (1985) 1.

U → ∞ phase diagram

$U = 4t_0$

FM SDW

CDW

Dimerized / BOW

$\dfrac{W}{t_0}$

$\dfrac{V}{t_0}$